

Organic-Inorganic Hybrids Using Novel Phenylethynyl Imide Silanes

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Introduction

Polyimides have been used in a wide variety of engineering applications such as microelectronic packaging, high temperature adhesives, and composites owing to their good thermal stability, excellent mechanical strength, dielectric insulation, and chemical resistance. The durability of an inorganic substrate bonded with a polyimide adhesive, however, has often failed to attain a level of performance required for many applications primarily due to the instability of the surface treatment on the inorganic substrate. Research has been focused on the development of a durable interfacial layer that can chemically bond with both the inorganic substrate and polyimide adhesive. Chemically-bonded polyimide-silica hybrids have been reported for microelectronic and corrosion resistant applications [1–3], where the organic and inorganic phases were able to mix at the molecular level. In this presentation, polyimide-silica hybrids using novel phenylethynyl imide silanes are reported. The phenylethynyl group is present in the organic precursor as either a pendent or an end group to bond chemically with the polyimide adhesive containing phenylethynyl groups during processing, while the silane group of the organic precursor would chemically react with the inorganic precursor through oxane bond formation. The chemical compositions of these novel hybrids were examined using X-ray mapping modes of scanning electron microscopy (SEM), which revealed a silicon gradient interphase between the high surface energy substrate and the polyimide adhesive. Novel aromatic phenylethynyl imide silanes (APEISs) and pendent phenylethynyl imide oligomeric disilanes (PPEIDSs) have been synthesized [4], and sol-gel solutions containing the new silanes, a phenylethynyl terminated imide oligomer (PETI-5), and an inorganic precursor were formulated to develop a gradient hybrid interphase between a titanium alloy and the adhesive. Two different sol-gel systems were investigated to develop organic-inorganic hybrids. Hybrid I was composed of an organic precursor containing both phenylethynyl and silane groups (PPEIDS) and an inorganic precursor. Functional group concentrations were controlled by the variation of the molecular weight of the imide backbone of PPEIDS. Hybrid II was composed of organic and inorganic precursors and a coupling agent containing both phenylethynyl and silane groups. Morphology and chemical composition of the hybrid interphase between the inorganic substrate and the adhesive were investigated, and the bond strength and durability were evaluated using lap shear tests at various conditions. The assessment of how the bonding at an interface is affected by various sol-gel solution compositions and environments is reported.

Experimental

Materials. The aromatic phenylethynyl imide silane monomer (APEIS) and the pendent phenylethynyl imide oligomeric disilane (PPEIDS) were synthesized [4], and the schematic chemical structures are presented in Figure 1. PETI-5 ($M_n = 5000$ g/mol) was used as received from Imitec, Inc. as a 35% (w/w) solution of the amide acid in N-methyl-2-pyrrolidinone (NMP). Tetraethoxysilane (TEOS, 98%, ACROS Organics) as the inorganic precursor and anhydrous NMP (Aldrich Chemical Co., Inc.) were used as received.

Hybrid sol-gel solutions. Organic and inorganic precursors with or without the coupling agent were mixed in NMP to form a transparent solution. Distilled water was added to hydrolyze the alkoxy silane groups. The sol-gel solution was stirred at least 12 hrs at room temperature before film casting or metal treatment. The major composition studied was 85 parts organic/ 15 parts inorganic (%w/w). The sol-gel hybrids I and II are composed of PPEIDS/TEOS and PETI-5/APEIS/TEOS, and the compositions are given in Table 1.

Films and lap shear specimens. The sol-gel solutions were cast on glass plates and dried to a tack-free form in a low-humidity chamber. The cast films were cured at 110 and 220°C for half an hour, and then 252 and 371°C for an hour in flowing air. The sol-gel solutions were also applied to titanium 6Al-4V alloy (Ti-6-4) by dipping, and the treated Ti alloy was dried at 110 and 220°C for half an hour. Lap shear specimens were bonded using FM-x5 (Cytec Fibrite, Harve de Grace, MD) polyimide adhesive tape in either a hydraulic press or an autoclave at 252°C and 371°C under pressure for one hour.

Characterization. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 at a heating rate of 10°C/min in static air with the glass transition temperature (T_g) taken as the inflection point of the ΔT vs temperature curve. Dynamic mechanical analysis (DMA) was performed in a tensile mode on film samples in flowing air at a heating rate of 2.0°C/min at 0.1, 1, and 10Hz. Thermomechanical analysis (TMA) was performed in a tensile mode in flowing air at a heating rate of 5°C/min. Thermogravimetric analysis (TGA) was performed in flowing air at a heating rate of 2.5°C/min. Scanning electron microscopy was performed using SEMs (Joel, JSM-5600 and 6400) to analyze the morphology of the interphase. X-ray photoelectron spectroscopy (XPS, Perkin Elmer 5400) and X-ray mapping and energy dispersive X-ray spectroscopy on an SEM were employed to determine the chemical composition of the hybrids. Auger electron spectroscopy (AES, Perkin-Elmer 610) was performed to determine the depth profile of the interphase. Thin film tensile properties were determined according to ASTM D882 using five specimens per test condition. Lap shear adhesive strengths were determined according to ASTM D1002 using four specimens per test condition.

Results and Discussion

Sol-gel hybrids I and II composed of PPEIDS/TEOS and PETI-5/APEIS/TEOS, respectively, were prepared in NMP and hydrolyzed by the addition of water prior to film casting or metal surface treatment. The sol-gel hybrids exhibited good thermal stability with 5% weight loss occurring above 480°C in flowing air. The T_g of the film of hybrid I was 314°C by DMA (0.1 Hz) and 305°C by TMA. The T_g of the analogous imide (PPEI) of the PPEIDS without disilane end groups was lower than that of the hybrid. This T_g increase of the hybrid may represent the degree of reaction between the disilane end groups of PPEIDS and TEOS. The modulus of hybrid I was also increased approximately 15% compared to that of the analogous imide. The T_g of hybrid II was 252°C by DSC and 248°C by TMA. For reference, the cured T_g of PETI-5 was 270°C. The T_g decrease of hybrid II was presumably due to chain extension between the phenylethynyl groups of PETI-5 and the monomeric APEIS and lack of siloxane bonding between the silane groups of APEIS and TEOS.

Lap shear strengths were measured at RT and RT after a 3-day water-boil (Table 2). Surface treatment of sol-gel hybrids I and II exhibited superior resistance after a 3-day water-boil as compared to a PETI-5 only treatment. The locus of the failure was either at the interface between the hybrid and the adhesive or in the adhesive tape cohesively, as seen in Figure 2. This implies that the interfacial strength between the metal substrate and the hybrid was higher than the cohesive strength of the adhesive. The interfacial strength between the hybrid and the adhesive tape can be improved by introducing more phenylethynyl moieties in PPEIDS. Lap shear strengths were measured at RT after aging unstressed specimens at 177°C in flowing air (Table 3). Both hybrids exhibited good strength retention even after 2000 hrs. The structure of the hybrid can be postulated by thermodynamics as well as kinetics. Since the metal substrate has a higher surface energy, the higher surface energy phase containing polar functional groups may diffuse near the metal substrate preferentially. If this diffusion occurs prior to substantial condensation reaction, a higher silica-like structure can develop near the metal substrate, since the silanol group has a higher surface energy than a siloxane group. Figure 3 shows an EDX line map of a cross-section of the hybrid I on a Ti 6-4 substrate. The silicon and carbon concentrations at the interface exhibit a compositional gradient hybrid structure. X-ray maps also reveal a higher silicon concentration near the metal substrate (Figure 4). Similar results were observed for hybrid II [5].

Conclusions

The Polyimide-silica hybrids using novel phenylethynyl imide silanes were studied as an interphase between a Ti alloy substrate and polyimide adhesive. Both hybrids studied exhibited excellent durability even after a 3-day water-boil or aging at 177°C. X-ray mapping modes using SEM were able to visualize the chemical composition distribution of the hybrid cross-section, which revealed the development of a silicon gradient hybrid structure between the metal and polyimide substrates. This gradient structure has contributed to the high strength and durability of the adhesive bond of the hybrids as compared to PETI-5 after exposure to a hot-wet environment.

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Table 1. General Compositions of Organic-Inorganic Sol-Gel Solutions

	Hybrid I	Hybrid II
Organic	PPEIDS	PETI-5
Inorganic	TEOS	TEOS
Coupling agent	None	APEIS

Organic:Inorganic = 85:15

Organic:NMP = 15:85

TEOS:H₂O = 1:1

Table 2. Lap Shear Strengths of Various Surface Treatments

Surface treatment	RT, psi (cohesive %)	RT after 3-d WB, psi (cohesive %)
Hybrid I	8800 ± 307 (95)	8108 ± 444 (91)
Hybrid II	6987 ± 342 (91)	6461 ± 175 (83)
PETI-5	7657 ± 571 (83)	4618 ± 435 (25)
PETI-5*	7100 (95)	5950 (35)

Surface pretreatment: sulfuric acid & alkaline perborate except *gritblast & PASA Jell-107.

Table 3. Lap Shear Strengths of Hybrid I after Aging at 177°C

	0 hr	500 hr	1000 hr
Exp #1	4254 ± 608 (35)	4976 ± 290 (54)	5040 ± 56 (54)
	0 hr	1500 hr	2000 hr
Exp #2	6162 ± 390 (50)	6835 ± 362 (75)	6027 ± 515 (53)

RT strength ± standard deviation, psi (cohesive failure mode, %)

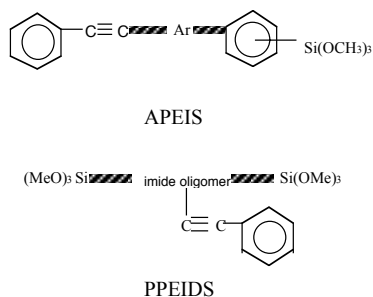


Figure 1. Schematic chemical structures of the novel phenylethynyl imide silanes.

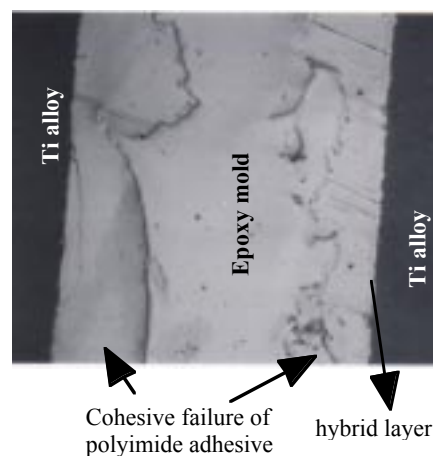


Figure 2. Optical micrograph of cross-section of the hybrid I after lap shear failure.

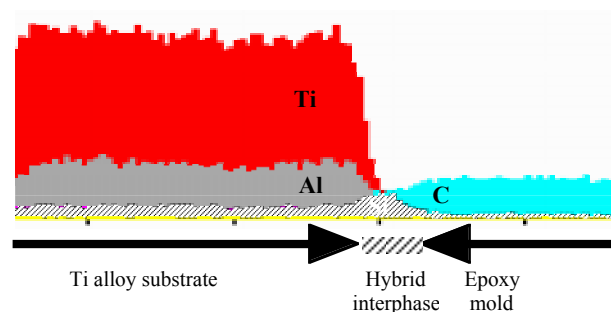


Figure 3. EDX line map of a cross-section of Ti alloy/hybrid I (PPEIDS/TEOS).

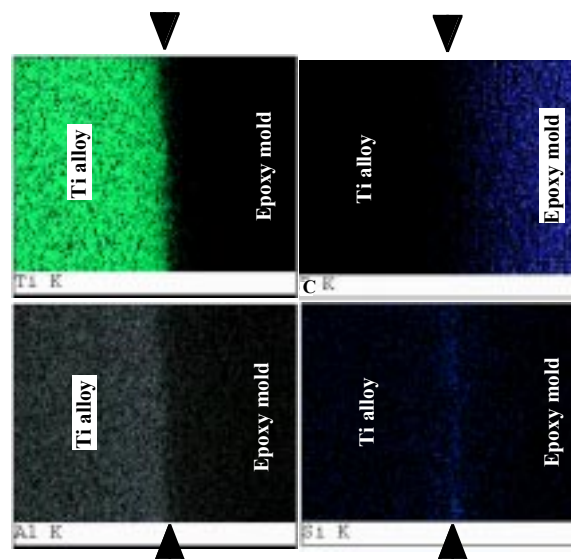


Figure 4. X-ray maps of a cross-section of Ti alloy/hybrid I (PPEIDS/TEOS). Arrows designate interphase layer.